

PATENT SPECIFICATION

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(54) PHOTOCROMIC FILTER FOR HUMAN SPECTACLES

(71) We, AMERICAN CYANAMID COMPANY, a corporation organised and existing under the laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in, and by the following statement:—

This invention relates to a sunlight activatable photochromic filter for human spectacles, in which a solid resinous matrix has dissolved in solid solution a photochromic material which undergoes a change in electronic configuration under the influence of activating radiation so as to give a different color and, in effect, a color-absorbing characteristic which makes the filter suitable for sunglass use.

The sunlight photochromic filter in accordance with this invention comprises a sunlight photochromic filter for human spectacles, comprising photochromic material dispersed at a total concentration of 5×10^{-2} to 1×10^{-3} moles per liter in a solid solution in a polymeric matrix which is solid at room temperature, which has a thickness of not more than 5 mm. and which is molecular oxygen-free (as hereinafter defined) and free from active centers capable of reacting with free radicals and biradicals, said photochromic material in the matrix being protected from atmospheric oxygen by an oxygen-impermeable barrier, said photochromic material comprising at least three components each of which is a compound, the molecules of which have a polynuclear conjugated aromatic ring system, which system has a set of electronic energy levels such that at least one of said levels is metastable and characterized by having strongly-allowed transitions from the metastable level to higher electronic states whose energy spacings relative to the metastable state correspond to energies of photons capable of exciting a visual response in the retina of the human eye, namely, whose wavelength is in the range of 400 to 750 nm., and which

metastable energy level is populated by producing a redistribution of the electrons such that the electronic configuration peculiar to the ground state is altered to the electronic configuration characteristic of the metastable state when the ground state molecules are subjected to excitation by photons having energies in the sunlight ultraviolet range of about 300 to 400 nm. and which molecules in the metastable state do not compete strongly for such sunlight ultraviolet photons, and the combination of photochromic components and polymeric matrix being such that the filter has a luminous transmission of 70% to 10% when activated by an activating radiation of 4.6 mW. per sq. cm. in the range of 300 to 400 nm. with both the activating and absorbed radiant energy normal to said matrix.

The thickness and weight of the sunlight filter must be acceptable to the user. This means a maximum filter thickness of the order of a few millimeters; any filter much more than 5 millimeters thick would be undesirably heavy and burdensome. A thickness of less than 1 millimeter for the photochromic matrix is preferred. For an all-plastics filter system, thicknesses up to 3 mm. at the lens center are acceptable.

In the vernacular of the user, spectacles containing sunlight filters are referred to as sunglasses whether the filters have glass layers or whether the filters are all plastics. As sunglasses, the dual meaning of filter lenses, whether part glass or all plastics is herein used. In speaking of a filter, the distinguishing terms of glass to indicate at least one glass layer, and plastics to denominate all plastics, though not necessarily only one layer or composition, are used.

Bright sunlight is used to designate the normal bright direct light from the sun, plus skylight, at noon, on June 21, in the latitude of Washington, D.C. on a clear day 30 minutes after a rain, as an accepted standard. This is taken to be 4.6 milliwatts per square centimeter between 300 nms. and 400 nms. Brighter sunlight is encountered at high altitudes, and particularly on a snowfield, or on a bright white sand beach. The intensity of

sunlight may be very low on a smogbound, overcast day, but as both the activating sunlight (U.V.) and the visible are reduced somewhat proportionately on such days, there is less need for darkening of the filter lenses, although some protection is still desirable.

The intensity of sunlight in the ultraviolet is comparatively limited. For example, the standard bright sunlight at noon under certain conditions is approximately 4.6 mW/per sq. cm., as stated previously. This corresponds to about 9×10^{17} quantum/cm² per second.

Because the number of activating photons is comparatively limited, there is competition between the various photochromic components which may be present in the ground state so that the extinction coefficients of various materials must be such that the darkening achieved is acceptably uniform across the spectrum. Additionally, the absorption spectrum in the triplet state must be such that the activated molecules do not compete unduly for ultraviolet radiation. The (T—T) absorption bands being in the blue and violet regions of the spectrum may encroach somewhat into the ultraviolet region because, of course, such bands are not completely sharp so that there is some competition for the ultraviolet radiation but for an acceptable sunglass, the combined spectrum of the photochromic components in the activated state is such that an adequate proportion of the activating ultraviolet is available to pump groundstate molecules into the activated triplet state. The rate relationships must be such that in bright sunlight a sufficient number of molecules are being pumped into the triplet state to replace those that decay from the triplet state back to the ground state, or which annihilates each other, and still give the required 30 to 90% darkening or 70 to 10% luminous transmission. The activity of the molecules must be such that at the low concentration dictated by the solubility of the photochromic components in the matrix, and the annihilation characteristics of the molecules, there still remains an adequate number of molecules in the triplet state in a layer of matrix not more than 5 mm. thick to give the desired darkening. Preferably, the activity should be such that a polymeric matrix of less than 1 mm. is sufficient for the desired darkening, although a 3 mm. layer is usually acceptable.

The multiple limitations and their interactions are such that the present selection of photochromic components is important in enabling achievement of adequate activity, stability, and other acceptable characteristics, including weight, cost, mechanical strength, and optical clarity, and uniformity to permit optical corrections.

The degree of darkening of sunglasses may be measured as the percent reduction in light

transmission although conveniently the degree of darkening is expressed in percentage of luminous transmission. For instance, a 30% darkening (luminous) would be 70% luminous transmission. Technically, such values may be measured at a specific wavelength and may be rated at such wavelength. However, where a wavelength is not specified, the values therein refer to the luminous transmission or darkening integrated over the visible spectrum from 400 to 750 nms. and weighted so as to indicate the transmission to a sensor possessing a wavelength sensitivity comparable to that of the "normal" human eye in bright light (so-called photopic sensitivity curve).

The photochromic layer may be augmented by a plastics or glass layer having additional filter characteristics. For some usages a polarizing layer is desired. A polarizing layer has useful characteristics when looking at reflected light on water, in automobile windshields, and other situations. It is often convenient to have a filter on the side of a photochromic matrix closest to the eye which will absorb both ultraviolet and infrared radiation to protect the eye from non-visible damaging electromagnetic radiation, without unduly influencing the photochromic action of the filter.

It is particularly desirable to avoid undue transmission near the ends of the visible spectrum, to which the eye has low sensitivity, and which may not cause the iris to contract, or "stop down", and yet be damaging to the retina.

The desired combination of filtering characteristics may be achieved by selecting filter layers having the appropriate augmenting characteristics.

Because the matrix polymer and glass may have rather similar indices of refraction, and dispersion curves, a matrix-glass filter sandwich may be manufactured in which only the glass surfaces contacting air are ground and polished to optical precision, with refraction correcting curvatures, for users requiring corrective lenses.

In all plastics filters, the outside plastics layers may be shaped to have refractory characteristics adapted to the specific corrections required by individual users by using suitably-shaped molds. The plastics may be ground to an optical correction, which is often a preferred method of shaping for small production runs. Other usual ophthalmic techniques are usable in connection with preparing the present photochromic filter systems for the user.

Theoretical aspects of the triplet state, particularly as it relates to reaction mechanisms are discussed at length in "Molecular Photochemistry", N. J. Turro, W. A. Benjamin Inc., New York 1967, Chapter 5 of which discusses intermolecular energy transfer.

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| | 2 | 3 | 1,419,985 | 3 |
| degree | 65 | | In accordance with the present invention, | 65 |
| age of | | | the molecules of polynuclear conjugated aromatic ring systems meeting requirements for | |
| a 30% | | | useful absorption in the metastable states are | |
| lumin- | 70 | 5 | stabilized at room temperatures — about | 70 |
| ies may | | | 20°C. — and over a range of at least arctic | |
| th and | | | to tropical temperatures by incorporating | |
| however, | | | them into a solid transparent matrix, which | |
| values | | | is free from reactive sites which would react | |
| mission | | 10 | with molecules in the very active triplet state, | |
| a spec- | 75 | | and deactivate them; and which matrix also | |
| ighted | | | excludes free molecular oxygen. | |
| sensor | | | Epoxy or polycarbonate resins and a poly- | |
| compar- | | 15 | meric phenyl siloxane resin sold by Owens, | |
| in eye | 80 | | Illinois, as glass resin 908 offer sufficient rigid- | |
| sitivity | | | ity, and dissolve the present photochromic | |
| nented | | | materials at low, but effective, concentrations, | |
| litional | | | and are therefore preferred materials for the | |
| polar- | | 20 | polymer matrix. | |
| er has | 85 | | For fast-acting photochromic effects by | |
| flected | | | triplet-triplet ($T-T$) absorption, in the | |
| ls, and | | | present filter, the energy absorbing electron | |
| o have | | | system in the triplet configuration results from | |
| matrix | | 25 | absorption of energy by a singlet configuration | |
| both | 90 | | at a shorter activating wavelength, then inter- | |
| protect | | | system crossing to a triplet configuration, fol- | |
| electro- | | | lowed by energy absorption at longer wave- | |
| fluenc- | | | length. Often, the intersystem crossing effi- | |
| er. | | 30 | ciency of the molecular structure in which the | |
| undue | 95 | | triplet configuration is desired is low, so that | |
| visible | | | a more effective intersystem crossing from | |
| itivity, | | | singlet to triplet electronic configuration is | |
| attract, | | | achieved by using one molecular structure or | |
| ng to | | 35 | chromophore system for achieving the inter- | |
| harac- | 100 | | system crossing from singlet to triplet followed | |
| filter | | | by transferring the triplet energy to a mole- | |
| enting | | | cular structure or chromophore which has a | |
| s may | | 40 | comparatively long triplet lifetime and effective | |
| 1, and | 105 | | absorption at the desired wavelength. | |
| sand- | | | If the energy is absorbed as singlet energy in | |
| ly the | | | molecular structure "D", and converted in | |
| 1 and | | | "D" by intersystem crossing to the triplet | |
| action | | 45 | state, and then transferred to structure "A", | |
| 3 cor- | 110 | | wherein the filtered light is absorbed, the | |
| lastics | | | process is called single energy transfer. If | |
| actory | | | absorbed by "A", transferred to "D" as singlet | |
| orrec- | | 50 | energy, crossed in "D" to triplet energy, and | |
| using | 115 | | then transferred back to "A", the process is | |
| ly be | | | called double energy transfer. | |
| often | | | Because of the complexity of the chemistry | |
| pro- | | 55 | and quantum mechanics involved, a full list | |
| tech- | 120 | | of all known compounds which give triplet | |
| epar- | | | absorption in the visible region, when acti- | |
| is for | | | vated, would unduly expand this specification. | |
| par- | | | Reference is made to United States Patent | |
| isms | | | No. 3,635,544, for some specific compounds. | |
| hoto- | 125 | 60 | Certain highly effective compounds are listed | |
| amin | | | herein. | |
| which | | | If the photochromic material is placed in | |
| | | | an optically-transparent matrix which, itself, | |
| | | | does not compete with the colorless version | |
| | | | of the active material for the exciting light | |
| | | | in the near ultraviolet (300—400 nm.), rapid | |
| | | | and reversible color development can be made | |
| | | | to occur as the population of the metastable | |
| | | | state is made to be large or vanishingly small | |
| | | | by the presence or absence of optical excita- | |
| | | | tion from radiation in the near ultraviolet | |
| | | | from direct sunlight and skylight. Optical | |
| | | | transparency and lack of color of the polymer | |
| | | | are thus both highly desirable. | |
| | | | The presence of excess or residual monomer | |
| | | | in the polymeric matrix is decidedly detrimental | |
| | | | to the achievement of photochromism when | |
| | | | it is governed by a mechanism involving | |
| | | | $T-T$ absorption. | |
| | | | Triplet molecules are also known as bi- | |
| | | | radicals because they possess two unpaired | |
| | | | electrons. As such, they are quite reactive and | |
| | | | can interact with each other, with oxygen, | |
| | | | or with any paramagnetic ion. A single un- | |
| | | | paired electron is responsible for the activity | |
| | | | of a free radical, with free radicals respon- | |
| | | | sible for many polymerization mechanisms. | |
| | | | A biradical could properly be called a double | |
| | | | free radical. Hence, the triplet molecules are | |
| | | | extremely reactive, and must be locked in | |
| | | | a non-reactive matrix to avoid prompt re- | |
| | | | action. Such prompt reaction would prevent | |
| | | | the desired photochromism. | |
| | | | Thus, it is necessary to employ a matrix | |
| | | | of good optical clarity that is free from: | |
| | | | residual monomer, plasticizers; and atoms, | |
| | | | molecules, ions or molecular fragments cap- | |
| | | | able of reacting rapidly with triplet molecules | |
| | | | or other metastable electronic state molecules, | |
| | | | which govern the photochromic effect here | |
| | | | disclosed. | |
| | | | The concentrations are critical for pre- | |
| | | | ferred sunlight results. The photochromic | |
| | | | molecules must be soluble in the matrix, | |
| | | | although the solution may be supersaturated. | |
| | | | The solution must be dilute, as the triplet | |
| | | | molecules react with each other resulting in | |
| | | | triplet-triplet annihilation. | |
| | | | The present filter can be prepared in the | |
| | | | absence of atmospheric oxygen or other mole- | |
| | | | cular oxygen source, or the oxygen can be | |
| | | | removed by vacuum, so as to leave the filter | |
| | | | molecular oxygen free, at the time of use. | |
| | | | By oxygen-free is meant that the amount | |
| | | | of molecular oxygen present is so small as | |
| | | | not to affect substantially the photochromic | |
| | | | action of the filter. If the molar concentra- | |
| | | | tion of oxygen is small, say less than 5% of | |
| | | | the molar concentration of the photochromic | |
| | | | material, the loss is small enough to be accept- | |
| | | | able. Even if the filter layer is not initially | |
| | | | free from oxygen, heating in vacuum permits | |
| | | | oxygen to diffuse out, to give an oxygen free | |
| | | | filter, at time of use. | |
| | | | If free (molecular) oxygen is present, or | |
| | | | if residual monomer is present in reactive | |
| | | | quantities, the $T-T$ absorption and filtering | |
| | | | effect is reduced, as the triplet form reacts, | |
| | | | instead of absorbing light. | |
| | | | The photochromic matrix layer of the | |
| | | | present filter is protected from molecular | |

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oxygen by a suitable barrier, which may take the form of protective layers of glass or other material through which gaseous oxygen does not diffuse. Thin layers of poly(vinyl alcohol), polyethylene terephthalate, poly(vinylidene chloride), regenerated cellulose or oxygen-proof high acrylonitrile content copolymer, for example "Barex"® 210 sold by Vistron Corp. give such protection. Use of a polymer for the oxygen barrier permits the use of all-plastics filters, which may have separate layers for oxygen protection and abrasion resistance. The filters may be formed with or without an optical correction for a specific user.

*"Barex" is a registered Trade Mark.

In the past, the traditional matrix for photochromic studies has been a frozen solution at 77°K, the temperature of liquid nitrogen. Solvents such as methylcyclopentane, tetrahydrofuran, or mixed solvents have been used. At 77°K diffusion of molecular oxygen is not a problem.

The present matrix system immobilizes the photochromic molecules in a polymer matrix at room temperatures.

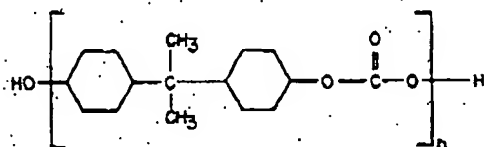
The present matrices enhance the lifetime of the triplet state as compared with polymethylmethacrylate (PMMA), which is not suitable for achieving the required luminous transmission characteristics as it is too soft:

Relative mean lifetimes of triplets in certain matrices.

| Temperature | Polycarbonate | Epoxy | PMMA |
|-------------|---------------|-------|------|
| at 77°K | 1 | 1 | 1 |
| at 25°C | 1 | 0.8 | 0.5 |

For the above results, the systems were free from molecular oxygen and unpolymerized monomer fragments, which could react with the triplet state molecules.

Suitable polycarbonates for use as the photochromic matrix may be exemplified by the product sold by General Electric Company under the registered Trade Mark "Lexan" which is a poly(4,4'-dioxidiphenyl-2,2-propane carbonate) of the formula:



wherein n is about 50 to about 200. The polymer is prepared by condensing bisphenol-A (4,4'-dihydroxy-diphenyl-2,2-propane) with phosgene, in the presence of a hydrogen chloride acceptor such as an amine base. The finely-divided photochromic components may be mechanically mixed with the finely-divided polycarbonate after which the mixture may be compression molded or injection

molded, for example in a nitrogen atmosphere to exclude oxygen.

The photochromic material may also be incorporated by dissolving both the photochromic material and the polycarbonate in a common solvent such as tetrachloroethane or methylene chloride and vaporizing the solvent by freeze drying so as to form a finely-divided molding powder which can be compression molded or injection molded.

Polycarbonates have a high transmittance of ultraviolet radiation as well as high transmittance in the visible, and essential freedom from color desired in the matrix. The polycarbonate has a high degree of activation at room temperature because the mean lifetime of the triplet molecules at room temperature is the same as it is at low temperature (78° Kelvin) thereby permitting a greater concentration of triplets to be pumped (and maintained) in the triplet state when using a light source (sunlight) of limited U.V. content.

Polycarbonates are sufficiently permeable to molecular oxygen so that the polycarbonate containing the photochromic material needs to be protected from atmospheric oxygen. The photochromic material in the plastics matrix is conveniently assembled for sealing between layers of glass or other molecular oxygen barrier material and then edge sealing. The assembly can be completed, and then sealed in an oxygen free atmosphere, such as nitrogen, or, after assembly, the filter assembly may be evacuated and kept in a vacuum until oxygen has diffused out of the polycarbonate, with nitrogen being used to break the vacuum; and then edge sealing with an oxygen barrier such as polyvinyl alcohol to protect around the edges of the filter. The glass may be selected for its radiation transmission characteristics so that in addition to protecting the photochromic material in the polycarbonate matrix, certain radiation is blocked by the glass. A glass that filters out infrared radiation is often preferred. For polymeric oxygen barrier, special layers of plastics may be added to effect transmitted light.

Epoxy resins are a developing class in which various organic compounds having an epoxy group are reacted with acid anhydrides or polyamides to form a solid which can serve as a matrix for the photochromic material in the present filters. The anhydride hardened resins are more apt to remain free from a yellowish color and hence are preferred. Because with epoxy resins, the hardener is both reactant and catalyst rather than only catalyst, the ratios and thoroughness of mix becomes more critical. The most readily available are epoxies based on the diglycidyl ether of bisphenol-A, from the reaction of bisphenol-A and epichlorhydrin. A typical low color epoxy

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resin such as Dow Epoxy Resin 332 has a Gardner color of 1, a molecular weight of 340—350, an epoxy equivalent of 173—179, and a viscosity of 3,600 to 6,400 centipoises at 25°C. Conventional hardening techniques may be used, as well known in the industry.

The brochure "Anhydride Hardeners for Epoxy Resins", Plastic Division Allied Chemical Co., P.O. Box 365, Morristown, New Jersey 07960, (1962) describes in considerable detail epoxy resins and anhydride hardeners.

A wide variety of epoxy resins can be used for the matrix, if special physical properties are desired for strength, or other reasons not pertinent to the photochromic aspects, a resin having such properties is chosen.

A catalyst or accelerator is useful to cause the resin to harden more rapidly and at a lower temperature. A self-hardening resin, that is one which hardens at room temperature, saves the cost of heating to cure.

Conveniently, the photochromic components are dissolved in the epoxy component so that when reacted with the hardening agent, the photochromic material is in solid solution in the transparent matrix. The epoxy matrix is more resistant to molecular oxygen than the polycarbonate matrix and hence can be cross-linked by reacting in air with the epoxy resins being placed between, for example, protective glass layers before hardening. The epoxy holds the glass layers together and can be edge sealed with polyvinyl alcohol after cutting to the size desired.

An alternative method of edge sealing is to coat the ground edges of the glass layers with a metallizing layer such as platinum, copper or silver, and reducing to the free metal on the ground glass by heating to increase adhesion, then after the glass layer assembly with the photochromic material in the photochromic matrix, the edge is soldered with a soft solder to give a hermetically sealed structure.

When polyvinyl alcohol is used for edge sealing, it is desirable to freshly grind the glass edge, and then clean the edge with acetone, then coat with polyvinyl alcohol, and let it set.

For eye glasses, it is convenient to form the assembly in the same oversize shape as current eye glasses blanks, then cut and grind the glass assembly to the desired size and shape, clean the edges with acetone, and coat with polyvinyl alcohol to give the polyvinyl alcohol edge seal.

As the cost of polishing a glass surface is considerable, glass layers may be used which are fine ground, and the polymeric matrix adheres thereto, and after the filter is formed, the air contacting surfaces only are polished to an optically acceptable surface. The filter may have a correction ground in, or be uncorrected for persons not needing corrections.

With polymeric oxygen barriers, the surfaces may be molded or otherwise shaped to the optically desired curvature.

For uniform darkening across the visible spectrum of 400 to 750 nm., at least three photochromic components are included. In a preferred embodiment there are at least three components (A), (B) and (C), as follows:

component (A), a photochromic material which, in the activated triplet state, appears yellow and hence absorbs in the blue region of the spectrum;

component (B), a photochromic material which, in the activated triplet state, appears pink, and hence absorbs in the yellow-green region of the spectrum; and

component (C), a photochromic material which, in the activated triplet state appears green and hence absorbs in the orange and red regions of the spectrum.

Because the absorption bands are broad, the exact colors vary, but the effective total gives a desired nearly gray shade of darkening. If darkening to some other shade is desired, a selection of concentrations to achieve such results may be chosen.

The following table of compounds includes effective sunlight activatable photochromic materials with values for τ_m , mean lifetime, and the photochromic color for given degrees of deuteration (the effect of deuteration on the properties of photochromic compounds is discussed in Canadian Patent No. 781,707).

TABLE I

| Compound | Degree of Deuteration | τ_m (sec) | P.C. Color |
|-------------------------------|-----------------------|----------------|------------|
| 1,2-5,6-Dibenanthracene | 90% or better | 7.5 | Pink |
| Picene | 90% or better | 10 | Gray-Green |
| 3,4-Benzotetraphene | 90% or better | 6.5 | Purple |
| 1,2-6,7-Dibenzopyrene | 90% or better | 20 | Pink |
| 1,2-3,4-5,6-Tribenzanthracene | 90% or better | 19 | Pink |
| 1,2-Benzocoronene | 90% or better | 21 | Blue-Gray |

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TABLE I (Continued)

| Compound | Degree of Deuteration | τ_m (sec) | P.C. Color |
|--|-----------------------|----------------|------------|
| 1,12-2,3-10,11-Tribenzoperylene-0 | | 7.5 | Tan |
| 1,2-5,6-Dibenzocoronene | 90% or better | 21 | Green |
| 1,2-3,4-5,6-Tribenzocoronene | 90% or better | 6.5 | Golden Tan |
| 1,2-3,4-6,7-12,13-Tetrabenzopentacene | 90% or better | 21 | Green |
| 1,2-3,4-5,6-7,8-Tetrabenzanthracene | 0 | 10.8 | Pink |
| 2-Phenyltriphenylene | 70% or better | | Yellow |
| 2-7-Diphenyltriphenylene | 70% or better | | Pink |
| 2-Xenyltriphenylene | 70% or better | | Pink |
| 2,2'-Bistriphenyl | 70% or better | | Pink |
| 2-Xenyl-7-phenyltriphenylene | 70% or better | | Green |
| 2-Paraterphenyltriphenylene | 70% or better | | Green |
| 7-Phenyl-2,2'-Bis-triphenyl | 70% or better | | Green |
| 2-Phenylphenanthrene | 90% or better | | Yellow |
| 2-7-Diphenylphenanthrene | 90% or better | | Pink |
| 2-Xenylphenanthrene | 90% or better | | Pink |
| 2,2'-Bisphenanthryl | 90% or better | | Pink |
| 2-Xenyl-7-phenylphenanthrene | 90% or better | | Green |
| 2-Paraterphenylphenanthrene | 90% or better | | Green |
| 7'-Phenyl-2,2'-Bisphenanthryl | 90% or better | | Green |
| p-terphenyl | 70% or better | | Yellow |
| 4-(4-paraterphenylmethyl)-benzophenone | | | |
| p-quaterphenyl | 70% or better | | Pink |
| 4-(4-paraquaterphenylmethyl)-benzophenone | | | |
| p-quinquephenyl | 70% or better | | Green |
| 4-(4-paraquinquephenylmethyl)-benzophenone | | | |
| naphtho[2,3-a]coronene | 100% | 3 | Green |

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The above compounds may have minor substituents, such as fluorine or a lower alkyl such as methyl without adversely affecting their photochromic characteristics. Usually such substituents add to the cost and have no advantages. For instance, 5 - fluorodibenz-[a,h] - anthracene is an exception and is preferred because the fluoro substituent permits equivalent photochromic action, but is not carcinogenic. The non-fluorinated compound is carcinogenic.

Representative embodiments of the invention are set forth in the following examples, in which all parts are by weight unless otherwise stated.

Example 1.

Epoxy Matrix And Glass Covers

For use in the bright sun, to protect across the entire visible spectrum, three or more photochromic materials are used, so that maximum absorbence of each is in a slightly different region, but in total, an absorbency pleasing to the eye is obtained. A set of such glasses is prepared by charging to a 2000 ml. round bottom flask having a small depression in the bottom to serve as an accumulating sump, 0.0473 gram of predeuterated benzo-[a]coronene (alternately numbered as 1,2 - benzocoronene), 0.0358 gram of perdeuterated dibenzo[a,g] - coronene (alternately numbered as 1,2 - 5,6 - dibenzocoronene), and 0.0324 gram of tribenzo[b,m,pqr]perylene (alternately numbered as 1,12 - 2,3 - 10,11 - tribenzoperylene); then adding 200 grams of chlorobenzene, by pouring down the side of the flask so as to wash all the crystals to the bottom.

The mixture is heated to boiling and rotated until a clear solution is formed. Then 35.52 grams of the diglycidyl ether of bisphenol A is added, and the mixture again heated, with rotation, until dissolved. The mixture is cooled to about room temperature, and slowly evacuated to avoid bumping. The flask is fitted to permit rotation, as a shell evaporator, and all of the chlorobenzene is evaporated using heat to about 70°C. while still under vacuum to assure complete removal.

To the solvent-free mixture is added 14.98 grams of vinylcyclohexene dioxide, and the flask rotated to assure uniform mixing. A mixture of 38.40 grams of 1,2 - cyclohexanedicarboxylic anhydride, 3.17 grams of phthalic anhydride, and 2.88 grams of 1,1,1 - trimethylol propane is added, and the flask again rotated until the mixture is homogeneous.

The thus-formed mixture may be used directly or filtered through a fritted glass disc.

A group of well cleaned 63 mm. and 71 mm. glass lenses of ophthalmic curvature, are placed with the distal lens facing down, with

spacers around the edge, 0.0195 inch thick. 1.52 Grams of the mixture is charged to the 63 mm. lenses, and 2.12 grams charged to the 71 mm. lenses, then the proximal glass layer of the same size is carefully lowered onto the spacers, being careful to eliminate air bubbles. The lenses are held together, while heating to 120°C. for 16.5 hours; 135°C. for 4 hours; 145°C. for 20 hours; then 165°C. for 1/2 hour; and allowed to cool to room temperature over 3 hours.

An assortment of correction curves is chosen with correction curves of strength and axis to fit a patient's prescription; the filter assembly cut to size and shape to fit selected frames, the edges ground with 600 mesh sandpaper, washed with acetone, coated with a 10% polyvinyl alcohol-water mixture, dried, cured at 55°C. for 1/2 hour, 75°C. for 1/2 hour, and at 100°C. for one hour.

In edge sealing, for maximum adherence of polyvinyl alcohol to the edge of a filter assembly, the edge of the assembly is freshly ground preferably with about a 600 mesh grit with the grinding including both layers of glass, and the polymeric matrix. The edge is washed with a volatile hydrophyllic organic solvent, such as acetone, ethanol, methanol or dioxane, or mixtures thereof, and air dried.

A solvent free from hydrophobic residues is needed. Reagent grade acetone gives excellent results, and is easily obtainable. The edges are then coated with a 10% polyvinyl alcohol in water mixture, permitted to air dry, or dried in an oven, and the assembly is ready for use. Whereas the polyvinyl alcohol layer alone is resistant to oxygen infusion, as shown by Oster, Nature 196, 1089, to 1090 (December 15, 1962), the grinding and solvent washing is required for adequate adherence to the edges of the filter assembly.

Polycarbonate and polymeric phenyl siloxane matrix filters need protection against oxygen more than the epoxy matrix filter.

The lens is then mounted in a frame.

The lens has shatter-resistant characteristics, so is a safety glass, has ophthalmic quality, and prescription corrections as chosen.

If clear glass lenses are chosen, the transmission in the visible spectrum at low light levels is over 90%. In bright June sun, noon, at Stamford, Connecticut, the luminous transmission drops to about 40%.

A proximal lens with greenish or greyish color and a luminous transmission of about 50% may be used if a lower transmission is desired. A thicker layer of the photochromic material, with appropriate concentration changes can be used if a greater photochromic darkening is desired.

For purposes of the present invention, the total concentration of photochromic components is 5×10^{-5} to 1×10^{-2} moles per liter of the polymeric matrix. At higher concentrations

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triplet-triplet annihilation reduces effectiveness, and at lower concentrations the matrix layer must be undesirably thick. Unless isomorphous, the presence of each photochromic component tends to increase the solubilities of the others.

Example 2.

Polycarbonate Matrix

A solution of 0.0473 gram of perdeuterated benzo[a]coronene, 0.0358 gram of perdeuterated dibenzo[a,g]coronene and 0.0324 gram of tribenzo[b,n,pqr] - perylene in benzene is freeze dried so as to yield a mixture of amorphous and microcrystalline product. This is mixed intimately with 95 grams of finely-powdered "Lexan" (registered Trade Mark) polycarbonate in an atmosphere of dry nitrogen. The resulting mixture is compression-molded in a dry nitrogen atmosphere to form clear disks having a diameter of 2" and a thickness of 2 mm., one of which is sealed between two Pyrex (registered Trade Mark) glass disks having a 2" diameter and thickness, each, of 1.5 mm. to protect the plastic from atmospheric oxygen and water vapor. When examined in ordinary artificial room-light, the disk is nearly colorless. When exposed to bright, noonday July sun at 41° north latitude on a clear day, the filter assembly shows darkening to about 35% luminous transmission.

Example 3.

Preparation of Higher Supersaturated Solutions

The solubility of the photochromic components in the matrix is one limitation on the concentration in preparing a photochromic filter. The multiple benzene rings in effect make the compounds closer and closer to the ring system believed to exist in certain forms of coal, and comparatively nearly as insoluble. Because of the great effectiveness, a very low concentration of the photochromic material is adequate, but sometimes a more dense thin filter is desired, which requires a greater concentration, and sometimes one which is either above the solubility limits of the photochromic material or one which requires a long time to dissolve in the matrix components.

By dissolving the components of the photochromic material and also one component of the plastic matrix in a common solvent, and evaporating the solvent, saturated solutions or even supersaturated solutions are readily obtained. Either benzene, or a substituted benzene such as chlorobenzene, or dichlorobenzene or toluene, is a solvent for both the photochromic components, and for a polymer component, such as the diglycidyl ether of bisphenol A.

The desired quantity of the photochromic

components is dissolved in sufficient analytical reagent grade of benzene to dissolve the photochromic components completely. For a small filter, from 3 to 10 milliliters of benzene is adequate, and in case of doubt a slight excess should be used to be certain that all of the photochromic components are completely dissolved to avoid leaving residual nuclei which would aid crystallization. After the photochromic material is dissolved in the benzene, which may be warmed to speed solution, there is added 0.5325 gram of the diglycidyl ether of bisphenol A (EPON 332) and the mixture agitated until homogeneous. Using a rotating evaporator, the solution is cooled to about 15°C. and vacuum applied while turning the container. Conveniently, the container is a small round bottom flask which has a slight depression blown into the bottom to serve as an accumulating point for the concentrate. While applying heat slowly, to avoid boiling, and hence spluttering or bumping, vacuum is applied and the benzene solvent is stripped off. After the solution becomes viscous, full vacuum is applied for about 5 minutes, and then while continuing heating to remove the last traces of the benzene, the flask is heated in hot water to about 100°C. This produces a supersaturated solution of the photochromic material in the epoxy.

A mixture is prepared of 0.408 gram of hexahydrophthalic anhydride, and 0.013 gram of phthalic anhydride, which mixture melts at room temperature, and is added to the epoxy. Then there is added 0.028 gram of trimethylol propane and the mixture stirred until homogeneous, under vacuum to avoid introducing air bubbles.

On a flat microscope slide is placed a 0.020 inch thick polycarbonate gasket and the molten mixture of the polymer containing the photochromic material is transferred to the middle of the slide, avoiding bubbles, with any bubbles being broken by a sharp stainless steel needle. A second slide is placed over the first and lowered so as to avoid bubbles between the two. The plates are clamped together with a polycarbonate gasket serving as a spacer, then cured at 120°C. for 24 hours after which a post-cure at 145°C. for 10 minutes is used after which the sample is permitted to cool. The sample thus formed is approximately one inch in diameter and is ready for study of its characteristics or use as a filter.

Quantities of the same photochromic materials as in Example 1, but using a 40% deuterated tribenzo[b,n,pqr] perylene were added to give the same concentrations as in Example 1.

The filter was found to turn darker than the filter of Example 1, showing a luminous transmission of about 25% in bright sunlight, and to clear a little more slowly.

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As so formed, with the reaction of the epoxy being aided by heat, atmospheric oxygen is effectively insoluble and hence the matrix as it polymerizes is oxygen free. After cooling, oxygen will slowly penetrate into the matrix. It may be removed by warming in vacuum, and for test purposes, it is convenient to accomplish the polymerization warm, and to store the filter matrix containing the photochromic material in solid solution in the epoxy resin in vacuum.

Epoxies show a high transmittance for ultraviolet radiation of an activating wavelength (300 to 400 nm.) and for the visible region (400 to 700 nm.).

Epoxies are mechanically rigid so as to minimize triplet-triplet annihilation at ambient temperatures below approximately 70°C.

Epoxy has an index of refraction close to that of ophthalmic glasses so that minimal additional refraction occurs as light passes the glass-epoxy interfaces.

Two previously ground and polished layers of glass, which may be lenses, can be fastened together to give an ophthalmic grade final filter assembly. Conveniently, the layer which is to be closest to the eye, or proximal layer, is concave towards the eye, the distal or outer layer is convex, and the two bonded faces of the glass layers are held firmly in place, and need only be fine ground, and need not be polished to form an ophthalmic grade lens blank.

The exposed surfaces of the lens blank may be shaped to a correction prescription after the glass layers are bonded, or before they are bonded. Obviously this is easier to do if two thick lens blanks are employed to make the sandwich. Bifocal or trifocal corrections are as readily ground into a three-layer filter as into a solid glass blank, and can be as optically perfect.

The epoxy matrix with two exposed glass layers inherently forms a safety glass, which minimizes the risk of eye injury by impact.

Epoxies reacted with an acid anhydride hardener tend to be clearer than those using amine hardeners, which at times have an undesirable yellow cast. Also the anhydride cured resins tend to be harder, and hence provide a firmer matrix for the solid solution. A small proportion of trimethylol propane serves as a catalyst, and also as a plasticizer, so that thermal and mechanical shock is less apt to crack the epoxy layer.

The glass layer closest to the eye may be made of a glass having infrared and/or ultraviolet filtering characteristics. The distal glass layer must pass the activating ultraviolet light, but can be of a glass which filters out infrared radiation.

Example 4.

The procedure of Example 2 was followed, but using 40% deuterated tribenzo[*b,p,q,r*]-perylene and twice the quantity of finely-divided polycarbonate (190 grams). Filters were formed using a 1 mm. thick photochromic layer. The luminous transmission in bright sunlight was less than 25%.

WHAT WE CLAIM IS:—

1. A sunlight photochromic filter for human spectacles, comprising photochromic material dispersed at a total concentration of 5×10^{-2} to 1×10^{-1} moles per liter in a solid solution in a polymeric matrix which is solid at room temperature, which has a thickness of not more than 5 mm. and which is molecular oxygen-free (as herein defined) and free from active centers capable of reacting with free radicals and biradicals, said photochromic material in the matrix being protected from atmospheric oxygen by an oxygen-impermeable barrier, said photochromic material comprising at least three components each of which is a compound, the molecules of which have a polynuclear conjugated aromatic ring system, which system has a set of electronic energy levels such that at least one of said levels is metastable and characterized by having strongly-allowed transitions from the metastable level to higher electronic states whose energy spacings relative to the metastable state correspond to energies of photons capable of exciting a visual response in the retina of the human eye, namely, whose wavelength is in the range of 400 to 750 nm.; and which metastable energy level is populated by producing a redistribution of the electrons such that the electronic configuration peculiar to the ground state is altered to the electronic configuration characteristic of the metastable state when the ground state molecules are subjected to excitation by photons having energies in the sunlight ultraviolet range of about 300 to 400 nm. and which molecules in the metastable state do not compete strongly for such sunlight ultraviolet photons, and the combination of photochromic components and polymeric matrix being such that the filter has a luminous transmission of 70% to 10% when activated by an activating radiation of 4.6 mW. per sq. cm. in the range of 300 to 400 nm. with both the activating and absorbed radiant energy normal to said matrix.

2. A filter according to Claim 1, in which said photochromic material comprises components (A), (B) and (C), component (A) being a photochromic material which, in the activated triplet state, appears yellow and hence absorbs in the blue region of the spectrum; component (B) being a photochromic

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- 10 material which, in the activated triplet state, appears pink, and hence absorbs in the yellow-green region of the spectrum; and component (C) being a photochromic material which, in the activated triplet state appears green and hence absorbs in the orange and red region of the spectrum.
3. A filter according to Claim 2, in which: Component (A) is: 1,2 - 3,4 - 5,6 - Tribenzocoronene, 1,12 - 2,3 - 10,11 - Tribenzoperylene, 4 - (4 - paraterphenylmethyl) - benzophenone, 2 - Phenyltriphenylene, or 2 - Phenylphenanthrene; Component (B) is: 1,2 - Benzocoronene, 2 - 7 - Di - phenyltriphenylene, 1,2 - 5,6 - Dibenanthracene, 3,4 - Benzotetraphene, 1,2 - 6,7 - Dibenzopyrene, 1,2 - 3,4 - 5,6 - Tribenzanthracene, 1,2 - 3,4 - 5,6 - 7,8 - Tetrabenzanthracene, 2 - Xenyl - triphenylene, 2 - 2' - Bistriphenyl, 2 - 7 - Diphenylphenanthrene, 2 - Xenylphenanthrene, 2 - 2' - Bisphenanthryl, 4 - (4 - paraquaterphenylmethyl)benzophenone, or 5 - fluorodibenz[*a,h*]anthracene; and Component (C) is: 1,2 - 5,6 - Dibenzocoronene, 1,2 - 3,4 - 6,7 - 12,13 - Tetrabenzopentacene, Picene, 2 - Xenyl - 7 - phenyltriphenylene, 2 - Paraterphenyltriphenylene, 7 - Phenyl - 2 - 2' - Bistriphenyl, 2 - Xenyl - 7 - phenylphenanthrene, 2 - Paraterphenylphenanthrene, 7' - Phenyl - 2 - 2' - Bisphenanthryl, 4 - (4 - paraquinquephenylmethyl)benzophenone, or naphtho[2,3 - *a*]coronene, including the at least partially deuterated forms thereof.
4. A filter according to Claim 2, in which the photochromic materials are: at least partially deuterated benzo[*a*]coronene, at least partially deuterated dibenzo[*a,g*]coronene, and at least partially deuterated tribenzo[*b,n,pqr*]perylene.
5. A filter according to Claim 2, in which the photochromic materials are: at least partially deuterated 5 - fluorodibenz[*a,h*]anthracene, at least partially deuterated dibenzo[*a,g*]coronene, at least partially deuterated tribenzo[*b,n,pqr*]perylene.
6. A filter according to any preceding claim, in which the polymeric matrix containing the photochromic material is an epoxy or polycarbonate resin.
7. A filter according to any preceding claim, in which the oxygen impermeable barrier is a layer of poly(vinyl alcohol), regenerated cellulose, polyethylene terephthalate, poly(vinylidene chloride) or high acrylonitrile polymer or combination thereof.
8. A filter according to any one of claims 1-6, in which the oxygen impermeable barrier is a layer of glass on each side of the polymeric matrix, which glass layers are edge sealed to prevent oxygen diffusion at the periphery, and the air contacting faces have a desired optical configuration.
9. A method of preparing a photochromic sunlight filter according to any one of claims 1 to 5, characterized by dissolving such photochromic components in a volatile solvent in such volume that said photochromic components are completely soluble therein, and also dissolving therein an epoxide component of a substantially transparent epoxy resin which shows a high transmittance in the ultraviolet region of 300 to 400 nm., the volume of said solvent being such that said epoxide is also completely soluble therein, evaporating said solvent by heat and reduced pressure, under conditions which avoid bumping and boiling until the said solvent is removed, thereby forming a super-saturated solution of said photochromic components in said epoxide, and before the photochromic components crystallize from the epoxide, adding a hardener, mixing until homogeneous, placing between optically transparent layers through which gaseous oxygen does not diffuse, and holding under a curing cycle until the epoxide and hardener react, thereby forming a stable hard epoxy resin matrix layer in which the molecules of the photochromic components are locked in solid solution, and which is protected from atmospheric oxygen by said optically transparent layer through which gaseous oxygen does not diffuse on each side.
10. A method of preparing a photochromic sunlight filter according to any one of Claims 1-5, characterized by dissolving a polycarbonate resin and such photochromic components in a solvent, placing the solution adjacent to a glass layer, and evaporating the solvent, thereby adhering the polycarbonate resin containing said photochromic components to the glass, covering with a second glass layer, thereby protecting the thus-formed polymeric matrix from exposure to atmospheric oxygen.
11. A method according to Claim 10, in which the air contacting faces of the two glass layer are ophthalmic grade, curved to a desired optical configuration adapted to possess a desired optical correction for human vision, and the three layer assembly is shaped to fit a spectacle frame, edge sealed, and assembled therein.
12. A method of preparing a photochromic sunlight filter according to any one of Claims 1-5, characterized by mixing solid finely-divided, thermoplastic polycarbonate resin and such photochromic components in solid, finely-divided form, heating until melted and substantially free from gaseous bubbles, and cooling until solid.
13. A method according to Claim 12, in which the said resin containing the photochromic components is injection molded, compression molded or cast to shape.
14. A method of preparing a photochromic sunlight filter according to any one of Claims 1-5, characterized by dissolving such photochromic components in a polymerizable car-

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 merizing the carbonate to form a filter lens
 of the desired shape, having a polycarbonate
 resin matrix.

5 15. A method of preparing a photochromic
 sunlight filter according to claim 1, substan-
 tially as described in any one of the Examples
 herein.

10 16. A photochromic sunlight filter according
 to claim 1, whenever prepared by a method

according to any one of claims 9 to 15.

17. Spectacles containing a pair of photo-
 chromic sunlight filters according to any one
 of claims 1 to 8 or claim 16.

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